



## Pure and Cupricated $\text{BaSnO}_3$ thick film resistor: Synthesis, Characterization and studies on its gas sensing performance

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*Submitted: Dec. 16, 2012*

*Accepted: Jan. 26, 2013*

*Published: Feb. 20, 2013*

*Abstract- In this work we report the synthesis, microstructure, electric properties and sensing performance of  $\text{BaSnO}_3$  (BS) powder, it was prepared by mechano-chemical method. As prepared powder is calcinated at temperatures 1100 °C, and 1300 °C tested for crystallization. Thick films were prepared using simple screen-printing technology. Structural and electrical analyses were performed and the results have been correlated. The material was tested for various gases such as  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NH}_3$ ,  $\text{Cl}_2$ ,  $\text{H}_2$ , LPG, ethanol, and  $\text{H}_2\text{S}$ . The pure BS film shows good response multiple gases at various operating temperature up to 500°C as  $\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{CO}$ , ethanol and,  $\text{H}_2\text{S}$  for different gas concentrations, when the pure film is surface modified with aqueous solution of  $\text{CuCl}_2$  using simple dipping technique for various time intervals (5 min., 10 min., 20 min. and, 30 min.), film improves the selectivity and sensitivity. Maximum response ( $S=36.2$ ) was found to  $\text{H}_2\text{S}$  gas at temperature of 250 °C and  $S=12.1$  for ethanol at 500 °C for gas concentration of 50 ppm with film dipped for 10 min. time interval. The characterization of the films was done by XRD, SEM and TG-DTA. Crystallite size, texture coefficient, specific surface area, electric properties and gas sensitivity of the films were measured and presented.*

*Index terms:  $\text{BaSnO}_3$  (BS); Thick films Resistor;  $\text{H}_2\text{S}$  gas sensor; Sensitivity; Selectivity.*

## I. INTRODUCTION

Alkaline-earth stannates (ASnO<sub>3</sub>, where A  $\frac{1}{4}$  Ca, Sr, Ba) are important materials for electronic industry due to their dielectric properties and some of their applications are thermally stable capacitors, humidity sensors, gas sensors, etc[1-3]. The interest in perovskite-type oxides is mainly due to the easy modification of their electric properties by the selection of an adequate cation and also due to their stability at high temperatures [4-5]. High sensitivity semiconductor gas sensors are strongly needed for measurement of physical quantities and for monitoring working environments. It was discovered that atoms and molecules interacting with semiconductor surfaces influence surface properties of semiconductors, such as conductivity and surface potential. Semiconductor oxides have been more successfully employed as sensing materials for the detection of different gases, such as CO, C O<sub>2</sub>, H<sub>2</sub>, alcohol, H<sub>2</sub>O, NH<sub>3</sub>, O<sub>2</sub>, NO<sub>x</sub>, etc. The gas sensing mechanism in all polycrystalline n-type semiconductors is generally ascribed to the Schottky barrier formation at gas-semiconductor interface, leading to a negative surface charge accumulation, typically O<sup>-</sup> ions. The variation of the height of the inter-granular barrier is the result of surface chemical reactions with environmental gases leading to electrical conductance modifications [5-8].

Among all the materials used for gas sensing purposes BaSnO<sub>3</sub> is most suitable due to its stability, porosity and repeatability. BaSnO<sub>3</sub> is found to be sensing many reducing gases CO, CO<sub>2</sub>, NO<sub>x</sub> at higher temperature [9-12]. As gas sensing is a surface phenomenon we could modify barium stannate film with some oxides so as to modify the performance [13-14]. More specifically, we aim at better information on: (i) the effectiveness of calcination temperature on particle size (ii) electronic properties and their changes in contact with reducing gases. Scanning Electron microscopy (SEM), X-ray diffraction (XRD) and specific surface area measurements were adopted to analyze the morphology, the crystalline structure and the mean grain radius. Finally, electrical measurements (electrical properties and gas sensing properties) have been performed.

## II. EXPERIMENTAL PROCEDURE

### a. Powder Preparation

The AR grade powders of  $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$  and  $\text{SnO}_2$  (with 1:1 molar concentration) were ball milled to mix thoroughly for 2h using planetary ball mill to obtain fine grained powder. Then hot water is added with constant stirring, followed by slow heating up to dryness. The powder was calcinated at  $1100^\circ\text{C}$  and,  $1300^\circ\text{C}$  for 6h [1-6]. The fined grain powder was obtained by milling in planetary ball mill for 2h. Powder was used to prepare thick film resistor and also for characterization. XRD spectrum of powders were analysed and confirmed the polycrystalline perovskite cubic phase. The as prepared powder was screen printed on glass substrate in the desired pattern.

### b. Paste and thick film preparation

The thixotropic paste was formulated by mixing the resulting fine powder BS with a temporary binder as a mixture of organic solvents [11-13]. The ratio of the inorganic to organic part was kept at 75:25 in formulating the paste. The thixotropic paste was then used to prepare thick films. The paste was screen- printed on a glass substrate in a desired pattern (1.5cm x 0.5cm). The films were fired at  $600^\circ\text{C}$  for 30 min. in air atmosphere to remove the residual.

### c. Gas sensing system

The sensing performance of the sensors was examined using a 'static gas sensing system' [10-13]. A constant D.C. voltage was applied across the film using two electrodes and current was measured by using digital Pico-ammeter. To heat the sample up to required operating temperatures the heater was fixed on the base plate. A thermocouple was connected to a digital temperature indicator. A gas inlet valve was fitted at one of the ports of the base plate. The required gas concentration inside the static system was achieved by injecting a known volume of test gas using a gas-injecting syringe. Air was allowed to pass into the glass dome after every gas exposure cycle.

## III. MATERIAL CHARACTERISTICS

### a. X-Ray Diffraction

Figure 1 depicts XRD pattern of BS powder. X-ray diffraction analysis of this powder was carried out in the 20-80 deg.(2 $\theta$ ) range using Cu-K $\alpha$  (with  $\lambda= 1.54\text{\AA}$ , 40 kV, 30mA) radiation. The observed peaks match well with the reported JCPDA data confirming the polycrystalline cubic perovskite phases. At 1100 °C calcinations XRD shown few smaller peaks related to BaCO<sub>3</sub> that was present in BaSnO<sub>3</sub> crystals but as calcination temperature was increased to 1300 °C BaCO<sub>3</sub> peaks disappeared and we get BaSnO<sub>3</sub> cubic form perovskite crystals. The intensities of an XRD pattern well match with cubic phase of BaSnO<sub>3</sub>.

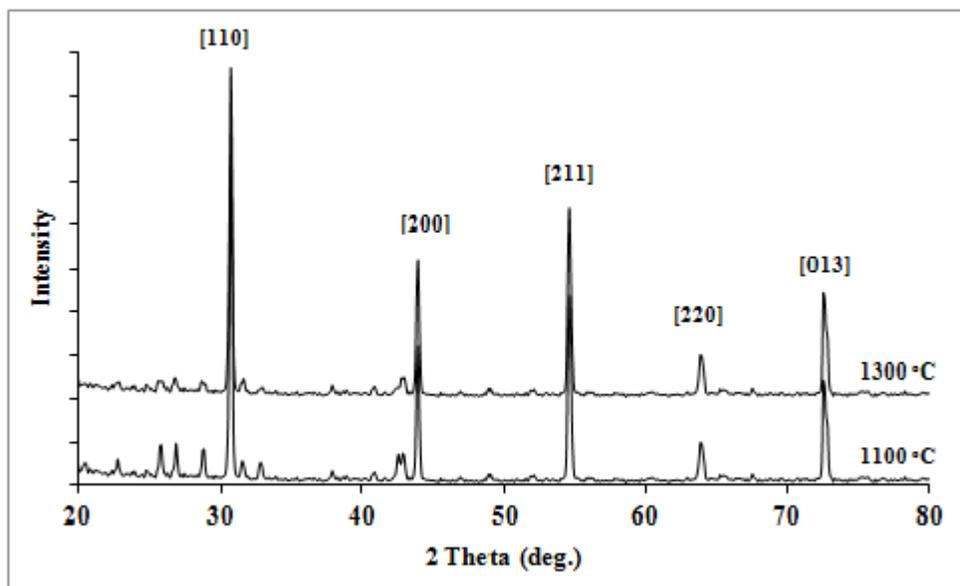


Figure 1. XRD pattern of pure BS powder calcinated at 1100 °C and 1300 °C

b. Calculation of structural parameters of the BS films

The Detailed knowledge of crystallite size and shape in a finely divided powder often helps to correlate many physical properties of a system undergoing transformation in a solid state reaction. The average crystallite size was determined based on XRD peak broadening using the Scherrer equation.

$$\text{—————} \quad (1)$$

Where D is average crystallite size,  $\beta$  is the broadening of the diffraction line measured at half maximum intensity (FWHM),  $\lambda$  is wavelength of the x- ray radiation and  $\theta$  is the Bragg angle.

The specific surface area of BS thick films was calculated using BET method by using the following equation [13]:

$$\text{---} \quad (2)$$

Where  $d$  is the diameter of the particles,  $\rho$  is the density of the particle and shape factor is 6. The specific surface area is total surface area divided by total volume of the particles, measured in  $\text{m}^2/\text{g}$ .

### c. Microstructure SEM

Figure 2 depicts the SEM images of (a) pure BS film, (b) Surface modified BS film with Copper oxide (dipping time 05 minutes) and (c) most sensitive surface modified BS film (dipping time 10 minutes). The modified film consists of voids and a wide range of particles with particle sizes ranging from 5 to 20 micrometer distributed non-uniformly. The surface modified film (with dipping time of 10 min) consists of uniform smaller particles associated with larger ones. These particles could be attributed to  $\text{CuO}_2$  particles.  $\text{CuO}_2$  grains may reside in the inter-granular regions of BS. Thus effective surface area was expected to be increased explosively.

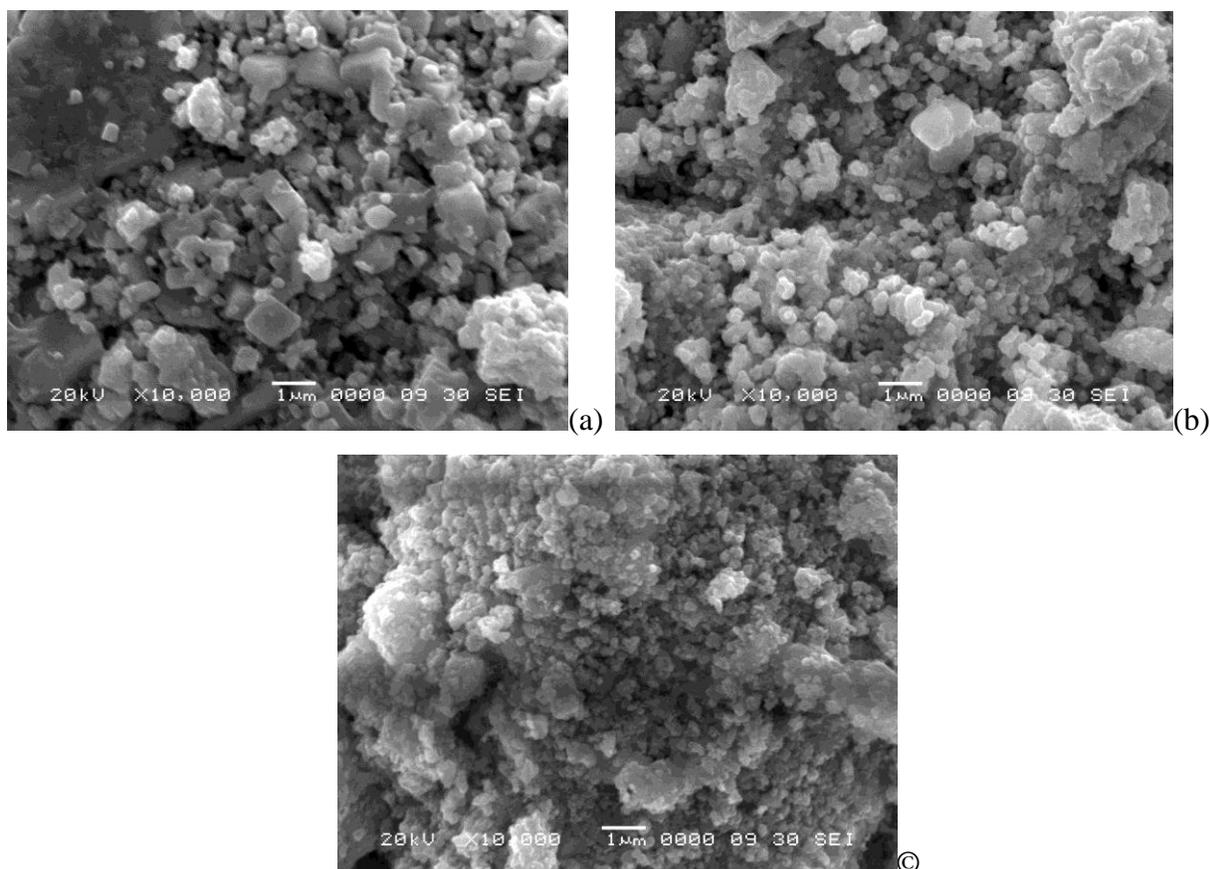


Figure.2.SEM images of (a) Pure BS, (b) CuO activated (05 min.) and (c) CuO activated (10 min.)

d. Elemental Analysis

The elemental composition, of Ba, Sn, O and Cu associated in the sensor element, was carried out using EDAX (JEOL, JED-2300, Germany) and is represented in Table 1. Modified BS films are observed to be more oxygen deficient than the pure BS film. This oxygen deficient would promote the adsorption of relatively large amount of oxygen species favorable for higher gas response. From elemental analysis (Table 1) of BS films, surface modified BS film for 10 min. dipping time was observed to be more oxygen deficient.

Table 1. Elemental analysis of pure and surface modified BS films

Element (Wt%)	Dipping Time in minutes				
	0 min.	05 min.	10 min	15 min.	30 min.
Ba	21.78	21.95	22.81	22.37	20.47
Sn	22.54	22.61	21.92	22.51	22.01
O	55.68	55.31	54.38	55.11	55.21
Al	0.0	0.13	0.89	1.01	2.31

e. Structural Parameters and their Analysis

Table 2 shows the crystallite size, particle size and specific surface area of the samples. The grain size is calculated using the Scherrer formula equation no (1). From XRD data of the calcinated powders texture coefficient is calculated which shows preferential orientation of the crystal. Specific surface area is calculated with equation no (2). The structural characteristics are summarized in Table 2. The modified BS film with dipping time 10 minutes is characterized by the small grain size of 29.46 nm and large active surface area (16.3 m<sup>2</sup>/g).

Table 2. Structural characteristics of pure and surface BaSnO<sub>3</sub> thick films

Sample	Crystallite(Grain) Size,	Particle Size,	Specific Surface
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	<b>D nm ( XRD)</b>	<b>d nm (SEM)</b>	<b>Area in m<sup>2</sup>/g</b>
Pure	41.51	400	6.9
Mod (10min)	29.46	125	16.3

f. Thermal stability of pure and surface modified BS sample

Thermo-gravimetric analysis (TGA) of samples was carried out using Mettler Toledo Star System - 851 from 10 to 900 °C in an air environment. The figure3 shows the TGA profiles of pure and surface modified BS films.

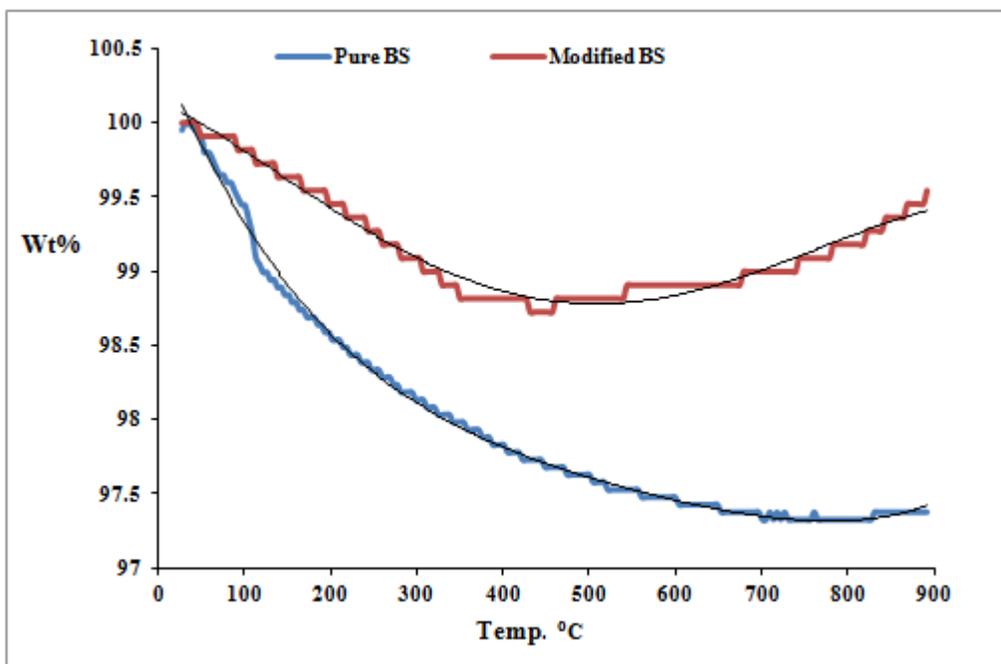


Figure.3. TGA of pure and surface modified BS films

It can be concluded from the figure that the surface modified BS film was more stable than pure BS. The weight loss in pure is more than surface modified sample for the temperature range 100°C to 400°C and there was a continuous gain in weight of the modified BS sample after 400°C, while the weight of pure sample decreased up to 700°C. The increase in weight of the surface modified sample (as compared to pure BS sample) would be attributing to the adsorbed oxygen content. The copper oxide on the surface BS sample would have formed misfit regions between the grains of BS and could act as efficient catalysts for oxygenation.

g. Thickness measurement

The thickness of the thick films was estimated by gravimetric weight loss method employing simple formula.

$$\text{---} \quad (3)$$

In equation (3) 't' is thickness of the film, 'A' is surface area of the film, 'σ' is average density of BS, and 'm' is change in weight of substrate before and after deposition. The thicknesses of the films were in the range from 65 to 90 μm. The reproducibility of the film thickness was achieved by maintaining the proper rheology and thixotropy of the paste.

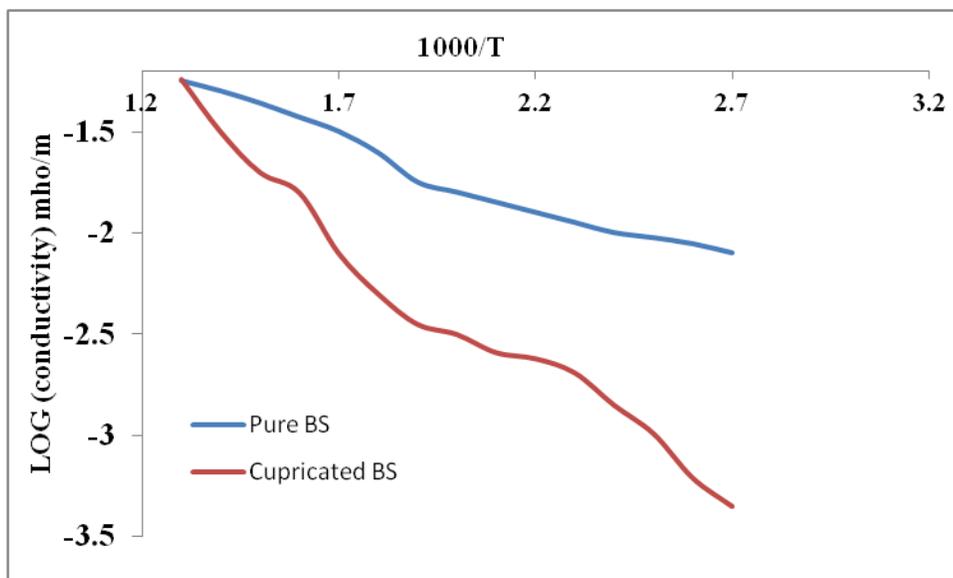
h. Thermoelectric power measurement

Semi-conductivity of all BS samples was confirmed by measuring thermo-electromotive force of the BS thick film samples. It was observed to be all samples of n-type material.

#### IV. ELECTRICAL PROPERTIES PURE AND SURFACE MODIFIED BS THICK FILM

a. Electrical Conductivity

Figure 4 represents the variation of conductivity with temperature of BS thick film. The conductivity of these films goes on increasing with increase in temperature, indicating negative temperature coefficient (NTC) of resistance. This shows the semiconducting nature of the films.



**Figure 4** Variation of Log of conductivity Vs  $1000/T$  °K in air for pure and cupricated BS films

## V. GAS SENSING PERFORMANCE OF FILMS

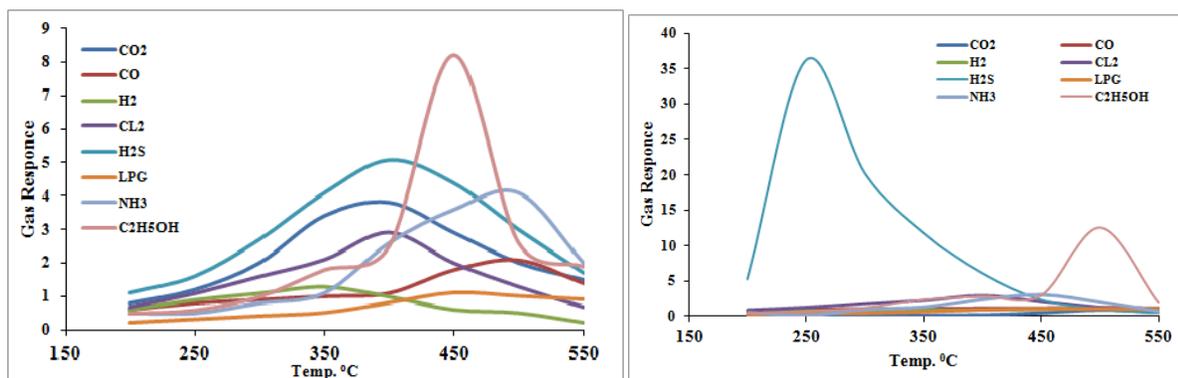
### a. sensing characteristics

The response (S) to the gas is defined as:

$$\text{—} \quad \text{Where} \quad (3)$$

$R_a$  is the sensor resistance in air and  $R_g$  is the resistance in the test gas at a given temperature [10]. The ability of a sensor to respond to certain gas in the presence of other gases is known as selectivity. The time taken for the sensor to attain 90% of the maximum change in resistance on exposure to the test gas is the response time. The time taken by the sensor to get back 90% of the original resistance is the recovery time. BS films were tested for gases such as CO, CO<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>S, Cl<sub>2</sub>, C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>, LPG at various operating temperature ranging from 150 to 450 °C and response of pure and surface modified films were plotted against temperature.

b. Gas sensing performance of pure and surface modified BS thick films

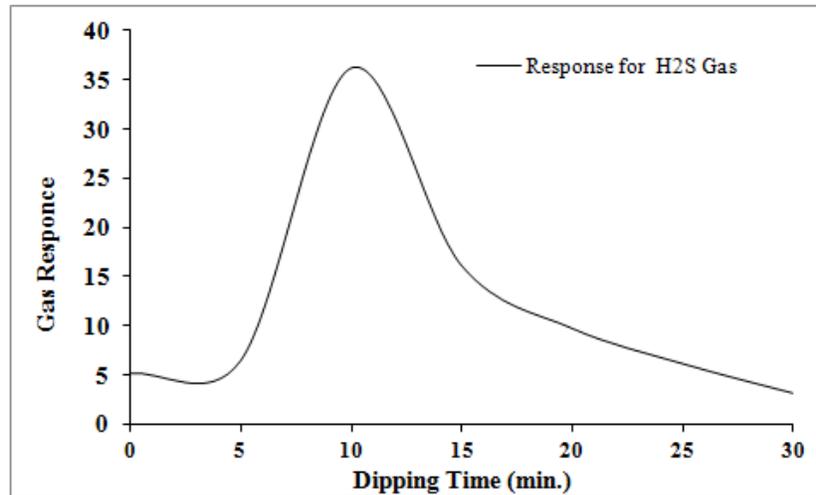


**Fig. 6.** Variation of gas response as a function of operating temperature (<sup>0</sup>C) for different gases of (a) pure BS film and (b) CuO modified BS film (10 min.)

Some features that can be drawn from these figures are:

- i. Each of the curves shows a maximum of the sensitivity corresponding to an optimum operating temperature of the sensor element. Pure and modified BS films, the sensitivity maximum appears at 450<sup>0</sup>C and 250<sup>0</sup>C respectively. Therefore, the sensors have need of thermal excitation to response to the investigated gases.
- ii. There are large differences in the sensitivity values to various gases of the pure and modified samples. Pure BS film shows a good response to ethanol and CuO - modified BS film shows response to H<sub>2</sub>S (fig.6). Figure 6(a) and (b) shows the variation of gas response of pure BS and CuO modified films (fired at 600<sup>0</sup>C) to various gases with operating temperature. The pure BS film shows good response (S=8.2) to ethanol at 450<sup>0</sup>C for gas concentration 400 ppm, (S=4.1) to NH<sub>3</sub> at 500 °C where as CuO-modified BS film improves the selectivity and sensitivity and maximum response (S=36.2) was found to H<sub>2</sub>S gas at 250<sup>0</sup>C for same gas concentration and it also improved ethanol response up to 12.1 at temperature of 500 °C .
- iii. It is clear from the data of elemental analysis that the modified films are observed to be more oxygen deficient and also more specific surface area (17.63m<sup>2</sup>/g) of BS film (dipped 10 min). This oxygen deficient and more surface area would promote the adsorption of relatively large amount of oxygen species favorable for higher gas response. Dipping time is also affecting the performance of the films.

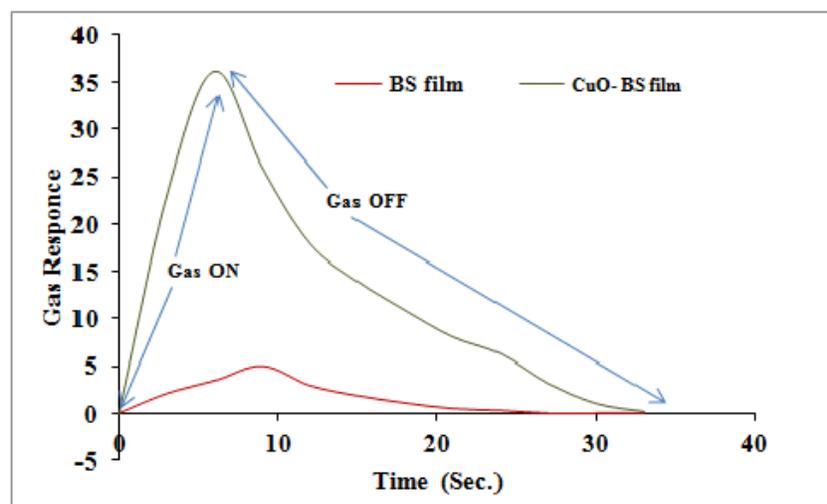
## c. Variation of Sensitivity with dipping time



**Fig. 7.** Variation in gas response to H<sub>2</sub>S with dipping

## d. Response and Recovery of pure and cupricated BS film to various gases

Response time (RST) is defined as the time required for sensor to attain the 90% of the maximum change in the conductance after exposure to the target gas on the surface of the film, while recovery time (RCT) is the time taken to get back 90 % of the initial value of the conductance once gas is made off. It was observed that RST is slightly higher for pure BS but when film is cupricated RST is improved. Similarly it was observed that RCT was increased in cupricated films.



**Fig. 8.** Response and Recovery time for pure BS and CuO-BS film for H<sub>2</sub>S gas

## VI. DISCUSSION

The gas sensing mechanism belongs to the surface controlled type which is based on the change of the electrical conductance of the semiconducting material upon exposure to different gases. The gas sensitivity is a function of grain size, surface state and oxygen adsorption. The surface modified films can be looked upon as the small particles of aluminum oxide distributed along the grain boundaries of BS. The H<sub>2</sub>S gas is reducing in nature. On exposure of H<sub>2</sub>S gas on the surface modified BS film, the sensor resistance decreases suddenly giving higher sensitivity. It can reduce Al<sub>2</sub>O<sub>3</sub> into Al<sub>2</sub>S<sub>3</sub> which are metallic in nature and is more conducting. This can be represented as:



Upon subsequent exposure of sensor to air ambient at elevated temperature, sulphides got oxidized and could be recovered back to oxides as



When oxygen is adsorbed on the surface of BS, abstracting electrons, and thus an increase in potential barrier at the grain boundaries. When reducing gas such as H<sub>2</sub>S is adsorbed between the grains of BS, the potential barrier decreases as a result of oxidative conversion of the H<sub>2</sub>S gas. H<sub>2</sub>S reacts with adsorbed oxygen ions as:



With this reaction, many electrons could release to thick film surface. This could make the Schottky surface barrier decrease; with the depletion layer thinner; consequently, the electrical conductance of the thin film increases. More gas would be adsorbed by the thin film surface; consequently, the gas sensitivity was enhanced. Increase in operating temperature causes oxidation of large number of H<sub>2</sub>S molecules, thus producing very large number of electrons. Therefore, conductivity increases to a large extent. This is the reason why the gas sensitivity

increases with operating temperature. However, the sensitivity decreases at higher operating temperature, as the oxygen adsorbates are desorbed from the surface of the sensor. Also, at higher temperature, the carrier concentration increases due to intrinsic thermal excitation and the Debye length decreases. This may be one of the reasons for decreased gas sensitivity at higher temperature.

## VII. SUMMARY AND CONCLUSIONS

The sensing mechanism of the BS was the “surface-controlled gas-sensing mechanism-(adsorption - desorption of oxygen)”. Barium stannet was prepared by solid state reaction (mechano-chemical) chemical method. Pure BS film has a good response to ethanol and  $\text{NH}_3$  gas and CuO-modified BS film has a good response to  $\text{H}_2\text{S}$  gas at optimum working temperature of  $500^\circ\text{C}$  and  $250^\circ\text{C}$  respectively. Modified film was selective and sensitive to  $\text{H}_2\text{S}$  gas; it can be due to fact that the film has maximum active surface area and smallest grain size as compared to pure film. The pure BS film shows good response ( $S=8.2$ ) to ethanol and  $\text{NH}_3$  at  $500^\circ\text{C}$  for gas concentration 50 ppm and CuO-modified BS film improves the selectivity and sensitivity and maximum response ( $S=36.2$ ) was found to  $\text{H}_2\text{S}$  gas at  $250^\circ\text{C}$  and improvement for ethanol to 12.1 at  $500^\circ\text{C}$  for same and or even smaller gas concentrations up to 50 ppm. It is clear from the data of elemental analysis that the modified BS film is observed to be more oxygen deficient, smaller grain size and more specific surface area ( $\text{m}^2/\text{g}$ ). This film could be more selective and sensitive to  $\text{H}_2\text{S}$ .

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